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(54) **AMPHIPHILIC MACROMOLECULE AND THE PURPOSE OF THIS AMPHIPHILIC MACROMOLECULE**

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USPC 526/263, 287, 305
See application file for complete search history.

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(57)   **ABSTRACT**

Amphiphilic macromolecules having structural units to adjust molecular weight and molecular weight distribution and charging property effects, high stereo-hindrance structural units, and amphiphilic structural units, are suitable for fields such as oil field well drilling, well cementation fracturing, oil gathering and transfer, sewage treatment, sludge treatment and papermaking, etc., and can be used as an oil-displacing agent for enhanced oil production, a heavy oil viscosity reducer, a fracturing fluid, a clay stabilizing agent, a sewage treatment agent, a papermaking retention and drainage aid or a reinforcing agent, etc.
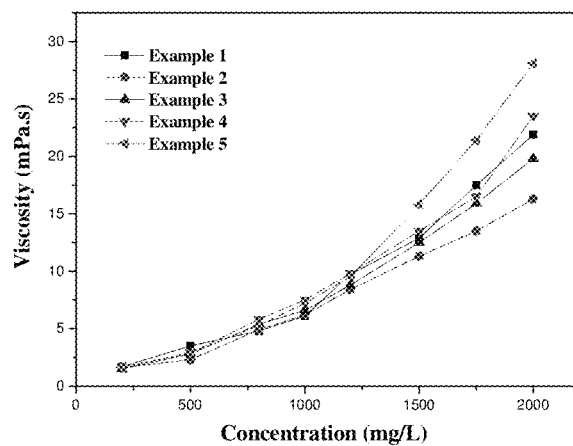
14 Claims, 1 Drawing Sheet

Figure 1: The relationship between the viscosity and concentration
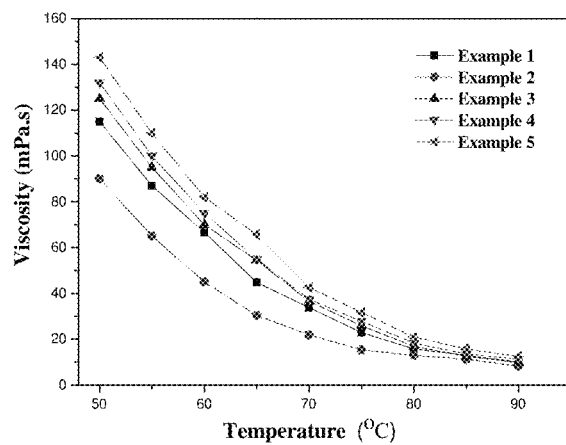

Figure 2: The relationship between the viscosity and temperature

AMPHIPHILIC MACROMOLECULE AND THE PURPOSE OF THIS AMPHIPHILIC MACROMOLECULE

CROSS-REFERENCE TO RELATED APPLICATIONS

This application is a national stage entry of PCT/CN2011/001577 filed Sep. 16, 2011, which claims priority to Chinese Patent Application No. 201110210343.7, filed on Jul. 26, 2011, said applications are expressly incorporated herein in their entirety.

TECHNICAL FIELD

This invention relates to an amphiphilic macromolecule and uses thereof, and this amphiphilic macromolecule is applicable to oilfield drilling, well cementing, fracturing, crude oil gathering and transporting, sewage treating, sludge treating and papermaking, and it can be used as intensified oil producing agent and oil displacing agent, heavy oil viscosity reducer, fracturing fluid, clay stabilizer, sewage treating agent, retention aid and drainage aid and strengthening agent for papermaking.

BACKGROUND OF INVENTION

Chemical process is an important Enhanced Oil Recovery technology for intensified oil production, and the chemical flooding is one of the most effective and potential measures, which is especially represented by polymer flooding. However, there arise some problems in the polymer system for conventional flooding with the deep implementation of polymer flooding technology. Under reservoir conditions of high temperature and high salinity, the viscosifying capacity and thermal stability of the widely used partially hydrolyzed polyacrylamide polymer reduces rapidly; in the meantime, the polyacrylamide polymer does not have the surface/interfacial reactivity per se, and could not start the oil film effectively, so that its ability to mine the remaining oil is limited. The polymer-based binary-component composite system (polymer/surfactant) and triple-component system (polymer/surfactant/alkali) may enhance the emulsification stability of the crude oil produced fluid, resulting in increased difficulty in oil/water separation and sewage treatment, as well as the weakening of synergistic effect between the components of the system under reservoir conditions, and also it may damage the reservoir. The application of the composite system is thus restricted.

Heavy oil recovery is a common difficulty around the world, mainly because the heavy oil is high in viscosity, high in gum asphaltene content or wax content, thus, the heavy oil is does not easily flow in the formation, wellbore and oil pipeline. Furthermore, since the oil-water mobility ratio is big, it can easily cause many problems such as rapid water breakthrough, high water content of produced fluid, and easy formation sand production. The process for heavy oil recovery can be mainly divided into recovery of liquid flooding (e.g., hot water flooding, steam huff and puff, steam flood and so on) and recovery of yield enhancement (e.g., horizontal well, compositing branched well, electric heating and etc). A Chemical viscosity reducer can disperse and emulsify the heavy oil effectively, reduces the viscosity of the heavy oil remarkably and decreases the flow resistance on heavy oil in the formation and wellbore, which is significantly important for reducing energy consumption in the process of recovery, decreasing discharging pollution and enhancing heavy oil recovery.
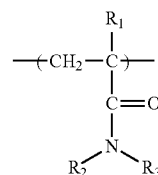
BRIEF DESCRIPTION OF THE INVENTION

In the following context of this invention, unless otherwise defined, the same variable group, and molecular and structural formula have the same definitions.

The instant invention relates to an amphiphilic macromolecule, this amphiphilic macromolecule has repeating units as described below: a structural unit A for adjusting molecular weight, molecular weight distribution and charge characteristics, a highly sterically hindered structural unit B and an amphiphilic structural unit C.

In an embodiment, the structural unit A for adjusting molecular weight, molecular weight distribution and charge characteristics comprises (meth)acrylamide monomer unit A_1 and/or (meth)acrylic monomer unit A_2. Preferably, the structural unit A includes (meth)acrylamide monomer unit A_1 and/or (meth)acrylic monomer unit A_2 simultaneously. In the art, the molecular weight of the amphiphilic macromolecule may be selected as needed, preferably, this molecular weight may be selected between 1000000-20000000.

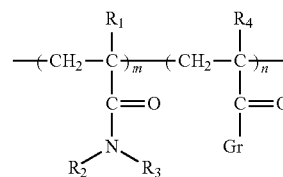Preferably, the (meth)acrylamide monomer unit A_1 has a structure of formula (1):

$$\text{formula (1)}$$

$$-\!\!\left(\!CH_2\!-\!\underset{\underset{\displaystyle R_2^{\nearrow}\!N\!\searrow R_3}{\overset{\displaystyle |}{\underset{\displaystyle C=O}{|}}}}{\overset{\displaystyle R_1}{\underset{\displaystyle |}{C}}}\!\right)\!\!-$$

In formula (1), R_1 is H or a methyl group; R_2 and R_3 are independently selected from the group consisting of H and a C_1-C_3 alkyl group; R_2 and R_3 are preferably H.

Preferably, the (meth)acrylic monomer unit A_2 is (meth) acrylic acid and/or (meth)acrylate. Preferably the (meth) acrylate is sodium methacrylate.

Preferably, based on 100 mol % of the entire amphiphilic macromolecule repeating units, the molar percentage of (meth)acrylamide monomer unit A_1 is 70-99 mol %; preferably 70-90 mol %, more preferably 73-78 mol %.

Preferably, the molar percentage of (meth)acrylic acid monomer unit A_2 in the whole amphiphilic polymer repeat unit is 1-30 mol %; preferably 1-25 mol %, and more preferably 20-25 mol %.

In another embodiment, the structural unit A for the regulation of molecular weight, molecular weight distribution and charge characteristics has a structure of formula (2):

$$\text{formula (2)}$$

$$-\!\!\left(\!CH_2\!-\!\underset{\underset{\displaystyle R_2^{\nearrow}\!N\!\searrow R_3}{\overset{\displaystyle |}{\underset{\displaystyle C=O}{|}}}}{\overset{\displaystyle R_1}{\underset{\displaystyle |}{C}}}\!\right)_{\!\!m}\!\!\left(\!CH_2\!-\!\underset{\underset{\displaystyle Gr}{\overset{\displaystyle |}{\underset{\displaystyle C=O}{|}}}}{\overset{\displaystyle R_4}{\underset{\displaystyle |}{C}}}\!\right)_{\!\!n}\!\!-$$

wherein, R_1 is H or a methyl group; R_2 and R_3 are independently selected from the group consisting of H and a C_1-C_3 alkyl group; R_2 and R_3 are preferably H; R_4 is selected from H or a methyl group; Gr is —OH or —O⁻Na⁺; m and n represent the molar percentages of the structural units in the entire amphiphilic macromolecule repeating unit, and m is 70-99 mol %, preferably 70-90 mol %, more preferably 73-78 mol %; n is 1-30 mol %, preferably 1-25 mol %, more preferably 20-25 mol %.

In another embodiment, in formula (2), R_1-R_3 are preferably H, and Gr is preferably —O⁻Na⁺.

In another embodiment, the highly sterically hindered structural unit B contains at least a structure G, wherein the

structure G is a cyclic hydrocarbon structure formed on the basis of two adjacent carbon atoms in the main chain, or is selected from a structure of formula (3), and the highly sterically hindered structural unit B optionally contains a structure of formula (4):
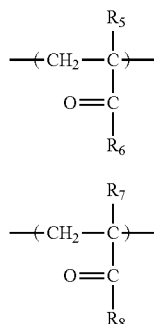
formula (3)

formula (4)

In formula (3), R_5 is H or a methyl group; preferably H; R_6 is a radical selected from the group consisting of the structures of formulas (5) and (6).

formula (5)

formula (6)

In formula (5), a is an integer from 1 to 11; preferably 1-7;

In formula (4), R_7 is H or a methyl group; R_8 is selected from the group consisting of —NHPhOH, —OCH$_2$Ph, —OPhOH, —OPhCOOH and salts thereof, —NHC(CH$_3$)$_2$CH$_2$SO$_3$H and salts thereof, —OC(CH$_3$)$_2$(CH$_2$)$_b$CH$_3$, —NHC(CH$_3$)$_2$(CH$_2$)$_c$CH$_3$, —OC(CH$_3$)$_2$CH$_2$C(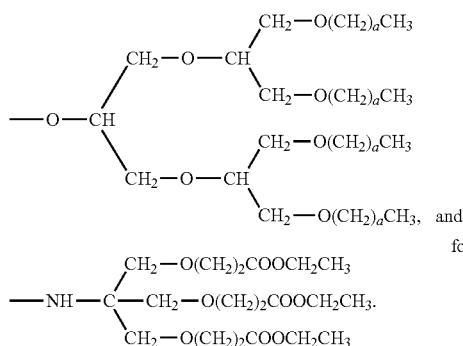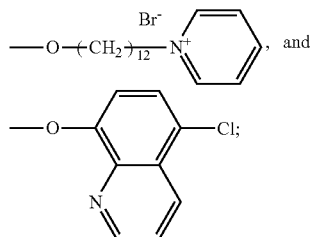CH3)$_2$(CH$_2$)$_d$CH$_3$, —NHC(CH$_3$)$_2$CH$_2$C(CH$_3$)$_2$(CH$_2$)$_e$CH$_3$, —O(CH$_2$)$_f$N$^+$(CH$_3$)$_2$CH$_2$PhX$^-$,

wherein b and c are respectively integers from 0 to 21, preferably from 1 to 11; d and e are respectively integers from 0 to 17, preferably from 1 to 7; f is an integer from 2 to 8, preferably from 2 to 4; and X$^-$ is Cl$^-$ or Br$^-$.

Preferably, the highly sterically hindered structural unit B comprises a structure G and a structure of formula (4).

In another embodiment, the cyclic hydrocarbon structure formed on the basis of two adjacent carbon atoms in the main chain is selected from the group consisting of:
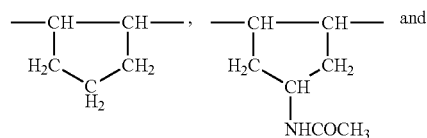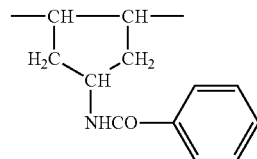
Preferably, the molar percentage of structure G of the highly sterically hindered structural unit B in the entire amphiphilic macromolecule repeating units is 0.02-2 mol %; preferably 0.02-1.0 mol %, more preferably 0.05-0.5 mol %.

Preferably, the molar percentage of the structure of formula (4) of the highly sterically hindered structural unit B in the entire amphiphilic macromolecule repeating units is 0.05-5 mol %; preferably 0.1-2.5 mol %, more preferably 0.1-0.5 mol %.

In another embodiment, the highly sterically hindered structural unit B has a structure of formula (7):
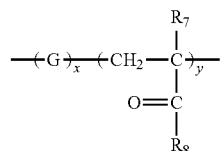
formula (7)

In formula (7), the definition on G is as described above, preferably the structure of formula (3),
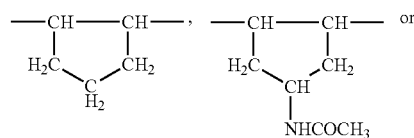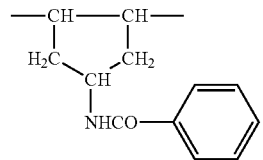
the definitions on R_7 and R_8 are as described in formula (4); x and y represent the molar percentages of the structures in the entire amphiphilic macromolecule repeating units, and x is 0.02-2 mol %, preferably 0.02-1.0 mol %, more preferably 0.05-0.5 mol %; y is 0.05-5 mol %, preferably 0.1-2.5 mol %, and more preferably 0.1-0.5 mol %.

In another embodiment, the amphiphilic structural unit C has a structure of formula (8):
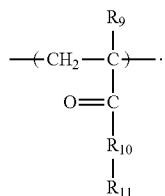
$$\text{formula (8)}$$

$$-(\text{CH}_2-\underset{\underset{\displaystyle R_{11}}{\overset{\displaystyle |}{\underset{|}{R_{10}}}}{\overset{\displaystyle |}{\underset{\|}{\overset{O=C}{\overset{|}{C}}}}})- \cdot$$

In formula (8), R_9 is H or a methyl group; R_{10} is —O— or —NH—; R_{11} is a radical containing a straight-chain hydrocarbyl, a branched hydrocarbyl, a polyoxyethylene (PEO) group, a polyoxypropylene (PPO) group, an EO and PO block, a mono-quaternary ammonium salt, a multiple-quaternary ammonium salt or a sulfonic acid and salts thereof.

Preferably, the molar percentage of the amphiphilic structural unit C in the entire amphiphilic macromolecule repeating units is 0.05-10 mol %; preferably 0.1-5.0 mol %, and more preferably 0.5-1.75 mol %.

In another embodiment, the structure consisted of R_{10} and R_{11} can be selected from —$O(CH_2)_gN^+(CH_3)_2(CH_2)_h$

CH_3X^-, —$NH(CH_2)_iN^+(CH_3)_2(CH_2)_jCH_3X^-$, —$O(CH_2)_k$ $N^+((CH_2)_pCH_3)_pX^-$, —$O(CH_2)_qN^+(CH_3)_2(CH_2)_\alpha CH$ $(SO_3H)CH_2(EO)_\beta(PO)_\gamma(CH_2)_\delta CH_3X^-$, —$NH(CH_2)_qN^+$ $(CH_3)_2(CH_2)_\alpha CH(SO_3H)CH_2(EO)_\beta(PO)_\gamma(CH_2)_\delta CH_3X^-$, —$O(CH_2)_qN^+(CH_3)_2(CH_2)_\alpha CH(COOH)CH_2(EO)_\beta(PO)_\gamma$ $(CH_2)_\delta CH_3X^-$, —$NH(CH_2)_qN^+(CH_3)_2(CH_2)_\alpha CH(COOH)$ $CH_2(EO)_\beta(PO)_\gamma(CH_2)_\delta CH_3X^-$, —$O(CH_2)_2N^+(CH_3)_2(CH_2)_\epsilon$ SO_3^-, —$(OCH(CH_2N^+(CH_3)_2(CH_2)_\zeta CH_3Cl^-)CH_2)_\eta O$ $(CH_2)_\theta CH_3$, —$(OCH(CH_2N^+((CH_2)_\lambda CH_3)_3Cl^-)CH_2)_\iota O$ $(CH_2)_\kappa CH_3$, —$OCH(CH_2N^+(CH_3)_2(CH_2)_rCH_3X^-))_2$, —$OCH(CH_2N^+((CH_2)_sCH_3)_3X^-))_2$;
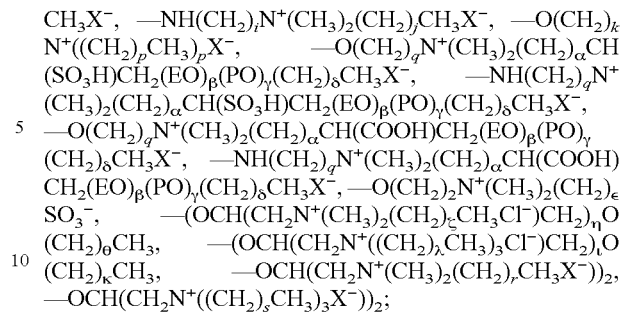
wherein, g, i, k and q are respectively integers of 1-6, preferably 2-4; h and j are respectively integers of 3-21, preferably 3-17; p is an integer of 3-9, preferably 3-5; α is an integer of 1-12, preferably 1-8; β and γ are respectively integers of 0-40, β is preferably 0-25, γ is preferably 0-15; δ is an integer of 0-21, preferably 0-17; ϵ is an integer of 4-18, preferably 4-12; ζ is an integer of 1-21, preferably 1-15; η and ι are respectively integers of 1-30, preferably 1-20; θ and κ are respectively integers of 3-21, preferably 3-17; λ is an integer of 0-9, preferably 0-5; r is an integer of 3-21, preferably 3-17; s is an integer of 3-9, preferably 3-5; and X^- is Cl^- or Br^-.

In another embodiment, the amphiphilic macromolecule has a structure of formula (9):
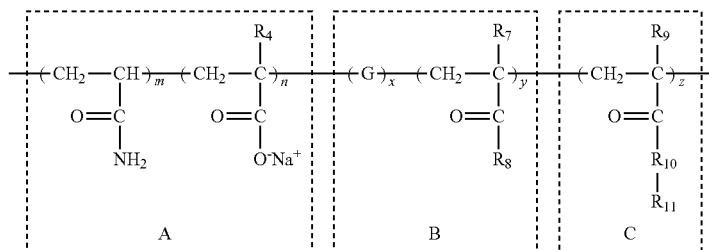
$$\text{formula (9)}$$

In formula (9), the definitions on R_4, m and n are as described in formula (2); the definitions on R_7, R_8, G, x and y are as described in formula (7); the definitions on R_9, R_{10} and R_{11} are as described in formula (8); z represents the molar percentage of this structural unit in the entire amphiphilic macromolecule repeat unit, and z is 0.05-10 mol %, preferably 0.1-5.0 mol %, more preferably 0.5-1.75 mol %.

Specifically, this present invention provides a high molecular compound having a structure of formulas (I)-(X):

$$\text{(I)}$$

-continued

(II)

A   B   C

(III)

A   B   C

(IV)

A   B   C

(V)

$\left(CH_2-CH\right)_m\left(CH_2-CH\right)_n$ $\left(CH_2-CH\right)_x$ $\left(CH_2-CH\right)_y$ $\left(CH_2-CH\right)_z$

A — B — C

(VI)

$\left(CH_2-CH\right)_m\left(CH_2-CH\right)_n$ $\left(CH-CH\right)_x\left(CH_2-CH\right)_y$ $\left(CH_2-CH\right)_z$

A — B — C

(VII)

$\left(CH_2-CH\right)_m\left(CH_2-CH\right)_n$ $\left(CH-CH\right)_x\left(CH_2-CH\right)_y$ $\left(CH_2-CH\right)_z$

A — B — C

-continued

(VIII)

(IX)

(X)
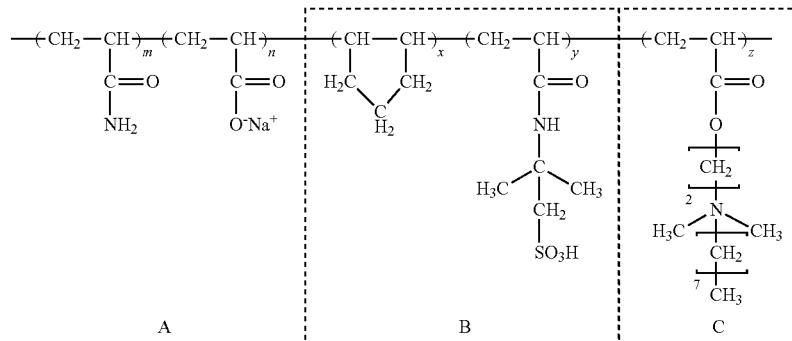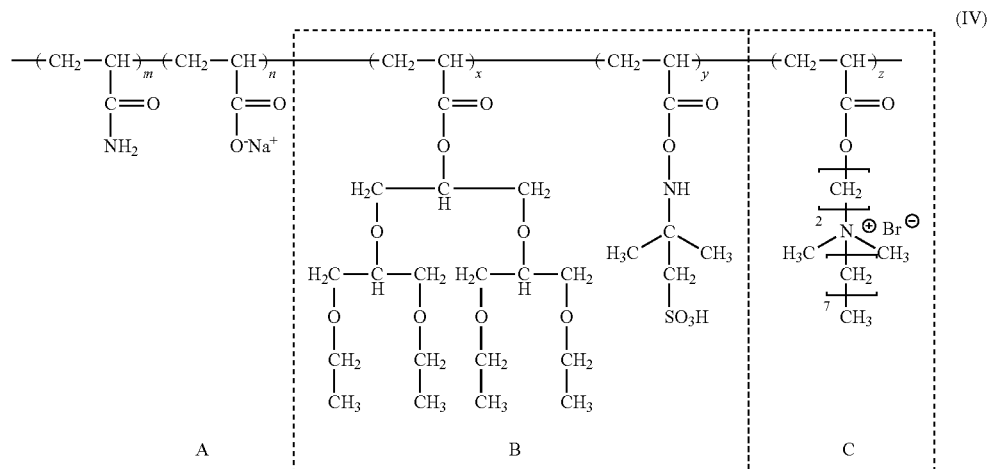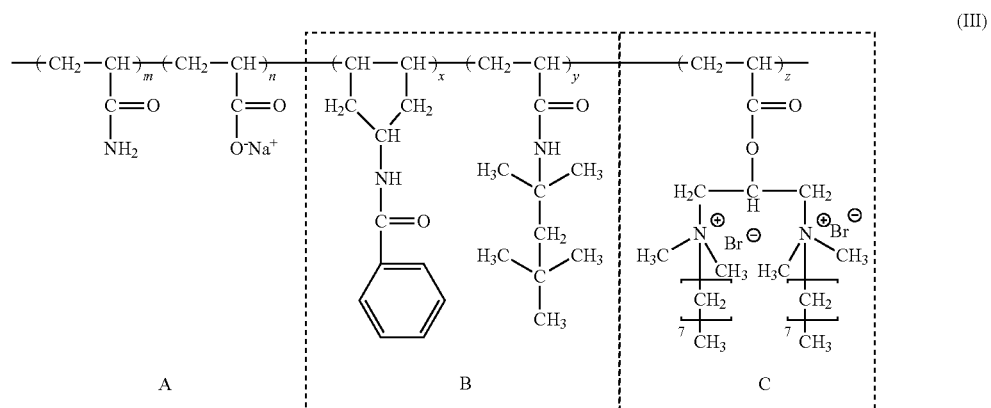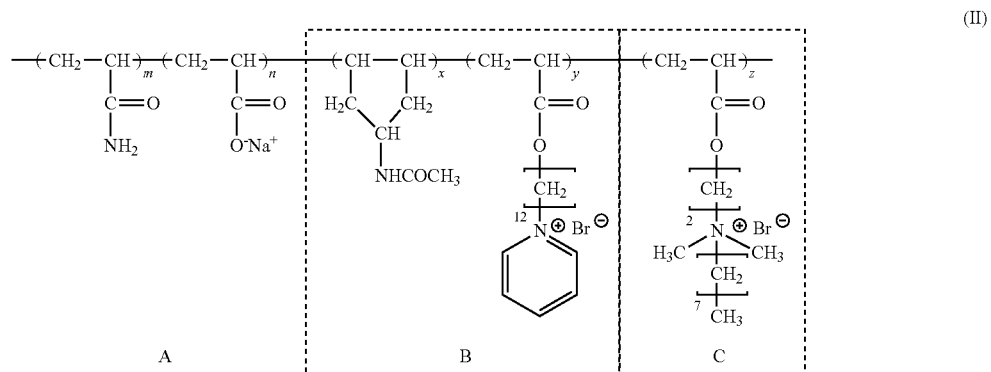
The molecular weight of the amphiphilic macromolecule described above is between 1000000 and 20000000; preferably between 3000000 and 13000000.

The measurement of the molecular weight M is as follows: The intrinsic viscosity [η] is measured by Ubbelohde viscometer as known in the art, then the obtained intrinsic viscosity [η] value is used in the following equation to obtain the desired molecular weight M:

$$M=802[\eta]^{1.25}$$

The amphiphilic macromolecule according to this present invention can be prepared by known methods in the art, for example, by polymerizing the structural unit for adjusting molecular weight, molecular weight distribution and charge characteristics, the highly sterically hindered structural unit

FIG. 2 depicts the relationship of viscosity vs. temperature of the amphiphilic macromolecules obtained from the examples 1-5 of the invention in saline having a degree of mineralization of 3×10^4 mg/L at the concentration of 1750 mg/L.

DETAILED DESCRIPTION OF THE INVENTION

The present invention is further illustrated below by combining specific examples; however, this invention is not limited to the following examples.

Example 1

This example synthesized the amphiphilic macromolecule of formula (1):

(I)

A   B   C
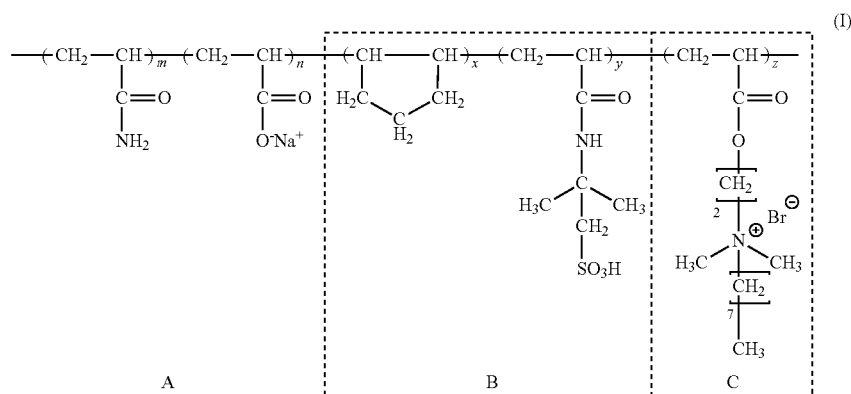
and the amphiphilic structural unit in the presence of an initiator. The polymerization process can be any type well known in the art, such as, suspension polymerization, emulsion polymerization, solution polymerization, precipitation polymerization, etc.

A typical preparation method is as follows: the above monomers are each dispersed or dissolved in an aqueous system under stifling, the monomer mixture is polymerized by the aid of an initiator under nitrogen atmosphere to form the amphiphilic macromolecule. The so far existing relevant technologies for preparing an amphiphilic macromolecule can all be used to prepare the amphiphilic macromolecule of this invention.

All the monomers for preparing the amphiphilic macromolecule can be commercially available, or can be prepared on the basis of prior art technology directly, and some monomers' synthesis are described in details in specific examples.

DESCRIPTION OF FIGURES

FIG. 1 depicts the relationship of viscosity vs. concentration of the amphiphilic macromolecules obtained from examples 1-5 of the invention in saline having a degree of mineralization of 3×10^4 mg/L at a temperature of 85° C.

The synthesis of the amphiphilic macromolecule of this example was as follows:

Firstly, water, accounting for ¾ of the total weight of the reaction system, was charged into a reactor, then various monomers, totally accounting for ¼ of the total weight of the reaction system, were charged into the reactor as well, and the molar percentages m, n, x, y, z for each repeating units were 78%, 20%, 0.25%, 0.5%, 1.25% in succession. The mixture was stirred until complete dissolution, and a pH adjusting agent was then added in to adjust the reaction solution to have a pH value of about 9, then nitrogen gas was introduced in for 30 minutes to remove oxygen contained therein. An initiator was added into the reactor under the protection of nitrogen gas, and nitrogen gas was further continued for 10 minutes, then the reactor was sealed. The reaction was conducted at a temperature of 25° C.; after 4 hours, the reaction was ended with a complete conversion. After the drying of the obtained product, powdered amphiphilic macromolecule was obtained. The molecular weight of the amphiphilic macromolecule was 1280×10^4.

Example 2

This example synthesized the amphiphilic macromolecule of formula (II).

(II)

The synthesis route of the monomer

was as follows:

The synthesis of the amphiphilic macromolecule of this example was as follows:

Firstly, water, accounting for ¾ of the total weight of the reaction system, was charged into a reactor, then various monomers, totally accounting for ¼ of the total weight of the reaction system, were charged into the reactor as well, and the molar percentages m, n, x, y, z for each repeating units were 75%, 23%, 0.15%, 0.1%, 1.75% in succession. The mixture was stirred until complete dissolution, and a pH adjusting agent was then added in to adjust the reaction solution to have a pH value of about 8, then nitrogen gas was introduced in for 40 minutes to remove oxygen contained therein. An initiator was added into the reactor under the protection of nitrogen gas, and nitrogen gas was further continued for 10 minutes, then the reactor was sealed. The reaction was conducted at a temperature of 20° C.; after 5 hours, the reaction was ended with a complete conversion. After the drying of the obtained product, powdered amphiphilic macromolecule was obtained. The molecular weight of the amphiphilic macromolecule was 1080×10^4.

Example 3

This example synthesized the amphiphilic macromolecule of formula (III):

(III)

The synthesis route of the monomer

was as follows:

The synthesis of the amphiphilic macromolecule of this example was as follows:

Firstly, water, accounting for ¾ of the total weight of the reaction system, was charged into a reactor, then various monomers, totally accounting for ¼ of the total weight of the reaction system, were charged into the reactor as well, and the molar percentages m, n, x, y, z for each repeating units were 75%, 24%, 0.25%, 0.25%, 0.5% in succession. The mixture was stirred until complete dissolution, and a pH adjusting agent was then added in to adjust the reaction solution to have a pH value of about 9, then nitrogen gas was introduced in for 30 minutes to remove oxygen contained therein. An initiator was added into the reactor under the protection of nitrogen gas, and nitrogen gas was further continued for 10 minutes, then the reactor was sealed. The reaction was conducted at a temperature of 25° C.; after 6 hours, the reaction was ended with a complete conversion. After the drying of the obtained product, powdered amphiphilic macromolecule was obtained. The molecular weight of the amphiphilic macromolecule was 590×10^4.

Example 4

This example synthesized the amphiphilic macromolecule of formula (IV):

(IV)

The synthesis route of the monomer

was as follows:

-continued

$$\text{KOH, Bu}_4\text{N}^+\cdot\text{IH}^- \xrightarrow{\quad\text{DCM}\quad}$$

$$\xrightarrow{\quad(CH_3)_2SO_4\quad}{K_2CO_3,\ DMF}$$

$$\xrightarrow{\quad H_2\quad}{Pd/C,\ EtOH}$$

$$\xrightarrow{\quad Br(CH_2)qCH_3\quad}$$

$$\xrightarrow{\quad NaOH,\ EtOH\quad}$$

$$\xrightarrow{\quad DCM,\ Et_3N\quad}$$

The synthesis of the amphiphilic macromolecule of this example was as follows:

Firstly, water, accounting for ¾ of the total weight of the reaction system, was charged into a reactor, then various monomers, totally accounting for ¼ of the total weight of the reaction system, were charged into the reactor as well, and the molar percentages m, n, x, y, z for each repeating units were 75%, 23%, 0.05%, 0.25%, 1.7% in succession. The mixture was stirred until complete dissolution, and a pH adjusting agent was then added in to adjust the reaction solution to have a pH value of about 9, then nitrogen gas was introduced in for 30 minutes to remove oxygen contained therein. An initiator was added into the reactor under the protection of nitrogen gas, and nitrogen gas was further continued for 10 minutes, then the reactor was sealed. The reaction was conducted at a temperature of 18° C.; after 6 hours, the reaction was ended with a complete conversion. After the drying of the obtained product, powdered amphiphilic macromolecule was obtained. The molecular weight of the amphiphilic macromolecule was 470×10^4.

Example 5

This example synthesized the amphiphilic macromolecule of formula (V):

(V)

A   B   C

The synthesis route of the monomer

was as follows:

-continued

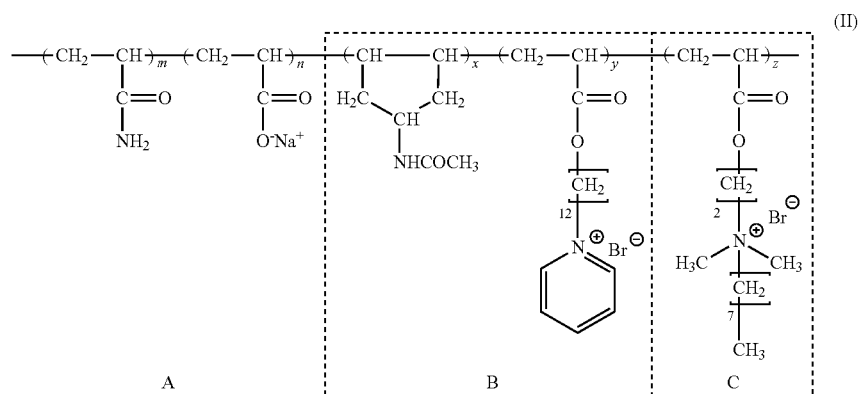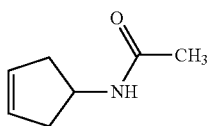The synthesis of the amphiphilic macromolecule of this example was as follows:

Firstly, water, accounting for ¾ of the total weight of the reaction system, was charged into a reactor, then various monomers, totally accounting for ¼ of the total weight of the reaction system, were charged into the reactor as well, and the molar percentages m, n, x, y, z for each repeating units were 78%, 20%, 0.1%, 0.25%, 1.65% in succession. The mixture was stirred until complete dissolution, and a pH adjusting agent was then added in to adjust the reaction solution to have a pH value of about 10, then nitrogen gas was introduced in for 30 minutes to remove oxygen contained therein. An initiator was added into the reactor under the protection of nitrogen gas, and nitrogen gas was further continued for 10 minutes, then the reactor was sealed. The reaction was conducted at a temperature of 25° C.; after 6 hours, the reaction was ended with a complete conversion. After the drying of the obtained product, powdered amphiphilic macromolecule was obtained. The molecular weight of the amphiphilic macromolecule was 530×10^4.

Example 6

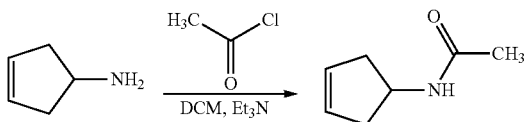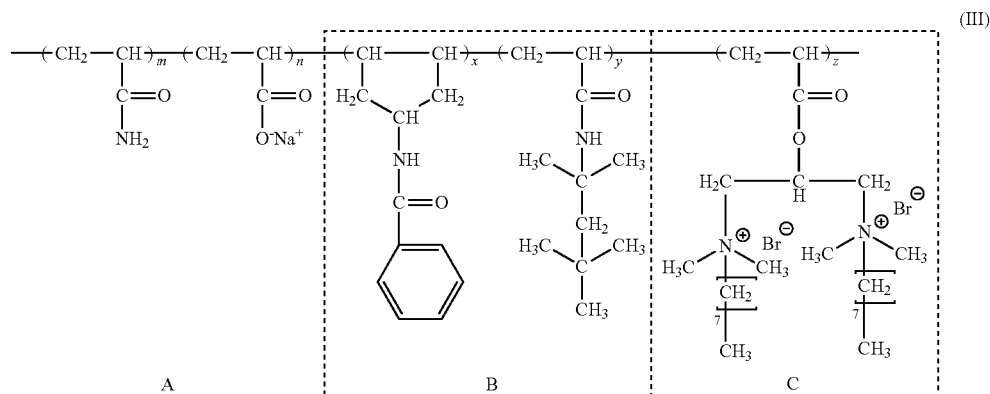This example synthesized the amphiphilic macromolecule of formula (VI):

(VI)

The synthesis of the amphiphilic macromolecule of this example was as follows:

Firstly, water, accounting for ¾ of the total weight of the reaction system, was charged into a reactor, then various monomers, totally accounting for ¼ of the total weight of the reaction system, were charged into the reactor as well, and the molar percentages m, n, x, y, z for each repeating units were 73%, 25%, 0.5%, 0.5%, 1% in succession. The mixture was stirred until complete dissolution, and a pH adjusting agent was then added in to adjust the reaction solution to have a pH value of about 8, then nitrogen gas was introduced in for 30 minutes to remove oxygen contained therein. An initiator was added into the reactor under the protection of nitrogen gas, and nitrogen gas was further continued for 10 minutes, then the reactor was sealed. The reaction was conducted at a temperature of 45° C.; after 3 hours, the reaction was ended with a complete conversion. After the drying of the obtained product, powdered amphiphilic macromolecule was obtained. The molecular weight of the amphiphilic macromolecule was 640×10^4.

Example 7

This example synthesized the amphiphilic macromolecule of formula (VII):

The synthesis of the amphiphilic macromolecule of this example was as follows:

Firstly, water, accounting for ¾ of the total weight of the reaction system, was charged into a reactor, then various monomers, totally accounting for ¼ of the total weight of the reaction system, were charged into the reactor as well, and the molar percentages m, n, x, y, z for each repeating units were 77%, 22%, 0.25%, 0.25%, 0.5% in succession. The mixture was stirred until complete dissolution, and a pH adjusting agent was then added in to adjust the reaction solution to have a pH value of about 9, then nitrogen gas was introduced in for 30 minutes to remove oxygen contained therein. An initiator was added into the reactor under the protection of nitrogen gas, and nitrogen gas was further continued for 10 minutes, then the reactor was sealed. The reaction was conducted at a temperature of 55° C.; after 2 hours, the reaction was ended with a complete conversion. After the drying of the obtained product, powdered amphiphilic macromolecule was obtained. The molecular weight of the amphiphilic macromolecule was 820×10^4.
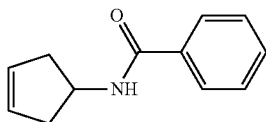
Example 8

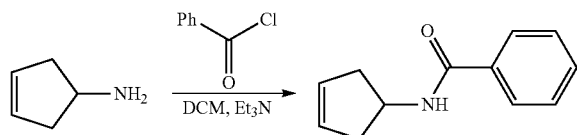This example synthesized the amphiphilic macromolecule of formula (VIII):

(VII)

(VIII)

$$-(CH_2-CH)_m-(CH_2-CH)_n-\mid-(CH_2-CH)_x-(CH_2-CH)_y-\mid-(CH_2-CH)_z-$$

A | B | C (structure VIII, repeating units with pendant groups including C=O, NH_2, O^-Na^+, NH, branched esters, and quaternary ammonium with $Br^{\ominus}$)

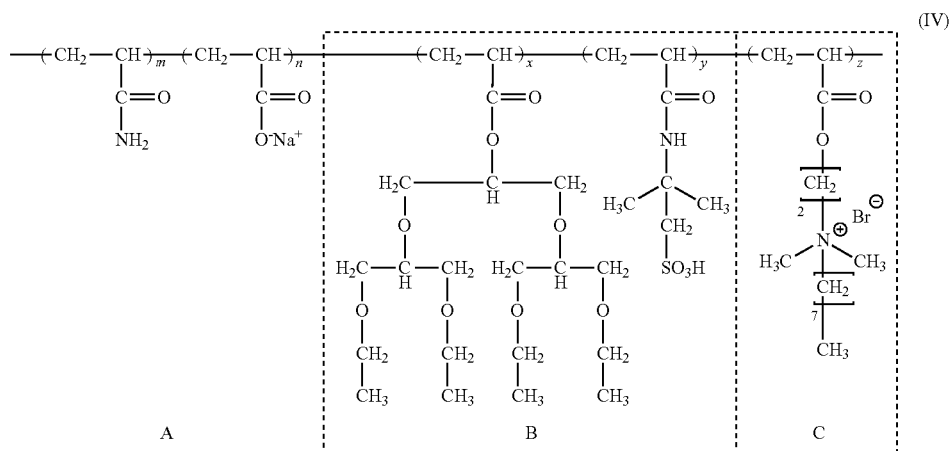The synthesis of the amphiphilic macromolecule of this example was as follows:

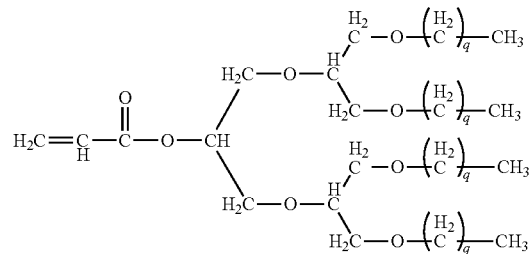Firstly, water, accounting for ¾ of the total weight of the reaction system, was charged into a reactor, then various monomers, totally accounting for ¼ of the total weight of the reaction system, were charged into the reactor as well, and the molar percentages m, n, x, y, z for each repeating units were 73%, 25%, 0.25%, 0.15%, 0.6% in succession. The mixture was stirred until complete dissolution, and a pH adjusting agent was then added in to adjust the reaction solution to have a pH value of about 10, then nitrogen gas was introduced in for 30 minutes to remove oxygen contained therein. An initiator was added into the reactor under the protection of nitrogen gas, and nitrogen gas was further continued for 10 minutes, then the reactor was sealed. The reaction was conducted at a temperature of 55° C.; after 3 hours, the reaction was ended with a complete conversion. After the drying of the obtained product, powdered amphiphilic macromolecule was obtained. The molecular weight of the amphiphilic macromolecule was 360×10^4.
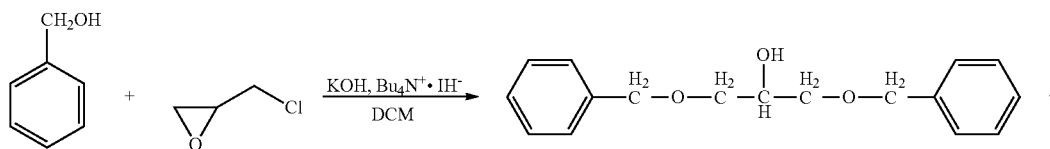
The synthesis of the amphiphilic macromolecule of this example was as follows:

Firstly, water, accounting for ¾ of the total weight of the reaction system, was charged into a reactor, then various monomers, totally accounting for ¼ of the total weight of the reaction system, were charged into the reactor as well, and the molar percentages m, n, x, y, z for each repeating units were 75%, 23%, 0.5%, 0.25%, 1.25% in succession. The mixture was stirred until complete dissolution, and a pH adjusting agent was then added in to adjust the reaction solution to have a pH value of about 8, then nitrogen gas was introduced in for 30 minutes to remove oxygen contained therein. An initiator was added into the reactor under the protection of nitrogen gas, and nitrogen gas was further continued for 10 minutes, then the reactor was sealed. The reaction was conducted at a temperature of 50° C.; after 2.5 hours, the reaction was ended with a complete conversion. After the drying of the obtained product, powdered amphiphilic macromolecule was obtained. The molecular weight of the amphiphilic macromolecule was 1260×10^4.

Example 9

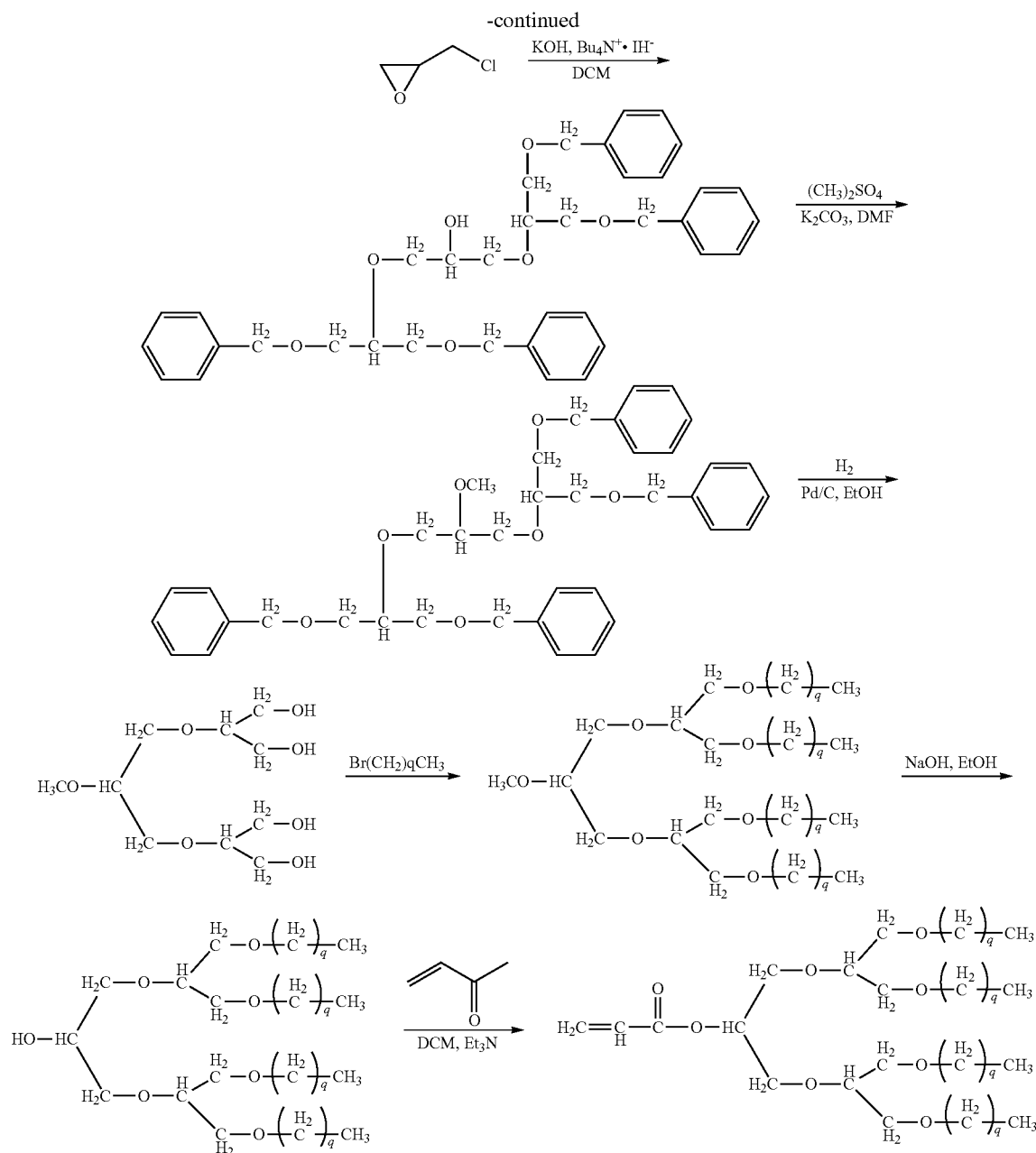This example synthesized the amphiphilic macromolecule of formula (IX):

Example 10

This example synthesized the amphiphilic macromolecule of formula (X):

(IX)

$$-(CH_2-CH)_m-(CH_2-CH)_n-\mid-(CH-CH)_x-(CH_2-CH)_y-\mid-(CH_2-CH)_z-$$

A | B | C (structure IX, repeating units with pendant groups including C=O, NH_2, O^-Na^+, $NHCOCH_3$, NH, SO_3H, and quaternary ammonium with $Br^{\ominus}$)
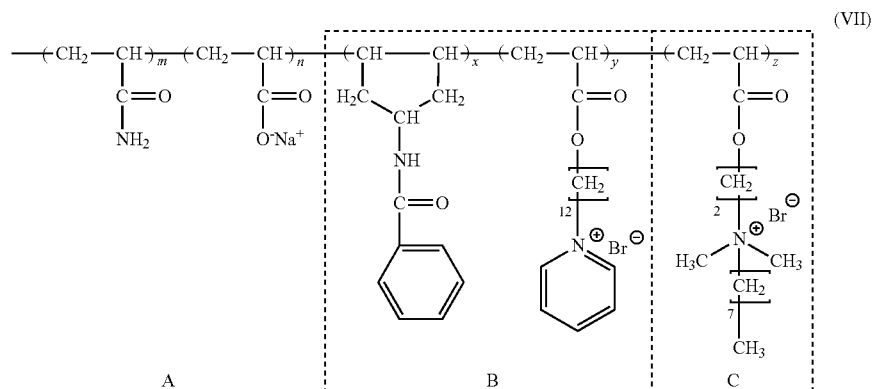
(X)

The synthesis of the amphiphilic macromolecule of this example was as follows:

Firstly, water, accounting for ¾ of the total weight of the reaction system, was charged into a reactor, then various monomers, totally accounting for ¼ of the total weight of the reaction system, were charged into the reactor as well, and the molar percentages m, n, x, y, z for each repeating units were 75%, 24%, 0.25%, 0.25%, 0.5% in succession. The mixture was stirred until complete dissolution, and a pH adjusting agent was then added in to adjust the reaction solution to have a pH value of about 8, then nitrogen gas was introduced in for 30 minutes to remove oxygen contained therein. An initiator was added into the reactor under the protection of nitrogen gas, and nitrogen gas was further continued for 10 minutes, then the reactor was sealed. The reaction was conducted at a temperature of 50° C.; after 4 hours, the reaction was ended with a complete conversion. After the drying of the obtained product, powdered amphiphilic macromolecule was obtained. The molecular weight of the amphiphilic macromolecule was $810×10^4$.

Measurement Examples

Measurement Example 1

Saline having a mineralization degree of $3×10^4$ mg/L was used to prepare amphiphilic macromolecule solutions with different concentrations, and the relationship between the concentration, temperature and the viscosity of the solution was determined. The results were shown in FIG. 1 and FIG. 2.

The figures showed that the amphiphilic macromolecule solutions of examples 1-5 still have favorable viscosifying capacity under the condition of high temperature and high degree of mineralization. The highly sterically hindered unit in the amphiphilic macromolecule reduced the rotational degree of freedom in the main chain and increased the rigidity of the macromolecule chain, which made the macromolecule chain difficult to curl and tend to stretch out, thus enlarging the hydrodynamic radius of the macromolecule; in the meantime, the amphiphilic structural unit associated each other to form the microdomain by intramolecular- or intermolecular-interaction, thus enhancing the viscosifying capacity of the solution remarkably under the conditions of high temperature and high salinity.

Measurement Example 2

Testing method: Under a testing temperature of 25° C., 25 ml electric dehydration crude oil samples from three types of oilfields were added in a 50 ml test tube with a plug, then 25 ml aqueous solutions of amphiphilic macromolecule with different concentrations formulated with distilled water were added in. The plug of the test tube was tightened, then the test tube was shaken manually or by using an oscillating box for 80-100 times in horizontal direction, and the shaking amplitude should be greater than 20 cm. After sufficient mixing, the plug of the test tube was loosed. Viscosity reduction rate for crude oil was calculated according to the following equation:

$$\text{Viscosity reduction rate}(\%) = \frac{\text{viscosity of crude oil sample} - \text{viscosity after mixing}}{\text{viscosity of crude oil sample}} \times 100$$

TABLE 1

Experimental results of the heavy oil viscosity reduction of the amphiphilic macromolecule obtained from the example 6 to example 10 (oil-water ratio 1:1, 25)

			Oil/water volume ratio (1:1) test temperature (25° C.)					
			oil sample 1	viscosity reduction rate (%)	oil sample 2	viscosity reduction rate (%)	oil sample 3	viscosity reduction rate (%)
			initial viscosity (mPa · s)					
			1500	—	4900	—	21000	—
Example 6	400	mg/L	625	58.33	1450	70.41	5200	75.24
	600	mg/L	410	72.67	1075	78.06	2850	86.43
	800	mg/L	300	80.00	875	82.14	1550	92.62
	1000	mg/L	275	81.67	650	86.73	1050	95.00
	1200	mg/L	250	83.33	575	88.27	925	95.60

TABLE 1-continued

Experimental results of the heavy oil viscosity reduction of the amphiphilic macromolecule
obtained from the example 6 to example 10 (oil-water ratio 1:1, 25)

		Oil/water volume ratio (1:1) test temperature (25° C.)					
		oil sample 1	viscosity reduction rate (%)	oil sample 2	viscosity reduction rate (%)	oil sample 3	viscosity reduction rate (%)
				initial viscosity (mPa · s)			
		1500	—	4900	—	21000	—
Example 7	400 mg/L	690	54.00	1550	68.37	5500	73.81
	600 mg/L	475	68.33	1125	77.04	2700	87.14
	800 mg/L	350	76.67	975	80.10	1650	92.14
	1000 mg/L	295	80.33	680	86.12	1100	94.76
	1200 mg/L	280	81.33	590	87.96	990	95.29
Example 8	400 mg/L	605	59.67	1275	73.98	4550	78.33
	600 mg/L	380	74.67	900	81.63	2350	88.81
	800 mg/L	275	81.67	650	86.73	1425	93.21
	1000 mg/L	250	83.33	550	88.78	975	95.36
	1200 mg/L	230	84.67	500	89.80	890	95.76
Example 9	400 mg/L	595	60.33	1250	74.49	4950	76.43
	600 mg/L	365	75.67	880	82.04	2750	86.90
	800 mg/L	250	83.33	675	86.22	1500	92.86
	1000 mg/L	225	85.00	575	88.27	1225	94.17
	1200 mg/L	210	86.00	510	89.59	1100	94.76
Example 10	400 mg/L	675	55.00	1325	72.96	4850	76.90
	600 mg/L	450	70.00	950	80.61	2375	88.69
	800 mg/L	340	77.33	705	85.61	1525	92.74
	1000 mg/L	295	80.33	585	88.06	1050	95.00
	1200 mg/L	270	82.00	525	89.29	875	95.83

Table 1 showed that the amphiphilic macromolecules of examples 6-10 had good effects for viscosity reduction as to all three oil samples. With the increase of the concentration of the amphiphilic macromolecule solution, the viscosity reduction rate increased. And, when the concentration of the amphiphilic macromolecule solution was the same, the viscosity reduction rate increased with the enhancing of the viscosity of the oil sample. It was believed that the amphiphilic macromolecule could reduce the viscosity of the crude oil remarkably via a synergetic effect between the highly sterically hindered structural unit and the amphiphilic structural unit, which could emulsify and disperse the crude oil effectively.
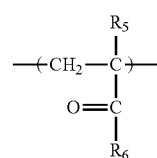
INDUSTRIAL APPLICATION

The amphiphilic macromolecule of this invention can be used in oilfield drilling, well cementing, fracturing, crude oil gathering and transporting, sewage treating, sludge treating and papermaking, and it can be used as intensified oil producing agent and oil displacing agent, heavy oil viscosity reducer, fracturing fluid, clay stabilizer, sewage treating agent, retention aid and drainage aid and strengthening agent for papermaking.

The amphiphilic macromolecule of this invention is especially suitable for crude oil exploitation, for instance, it can be used as an intensified oil displacement polymer and a viscosity reducer for heavy oil. When it is used as an oil displacement agent, it has remarkable viscosifying effect even under the condition of high temperature and high salinity, and can thus enhance the crude oil recovery. When it is used as a viscosity reducer for heavy oil, it can remarkably reduce the viscosity of the heavy oil and decrease the flow resistance thereof in the formation and wellbore by emulsifying and dispersing the heavy oil effectively.
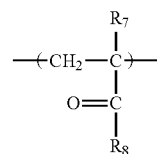
What is claimed is:

1. An amphiphilic macromolecule comprising: as repeating units, a structural unit A for adjusting molecular weight, molecular weight distribution and charge characteristics, a highly sterically hindered structural unit B and an amphiphilic structural unit C,

wherein the highly sterically hindered structural unit B contains at least a structure G, wherein the structure G is a cyclic hydrocarbon structure formed on the basis of two adjacent carbon atoms in the main chain, or is selected from a structure of formula (3), and the highly sterically hindered structural unit B optionally contains a structure of formula (4):

formula (3)

$$-\text{(CH}_2-\text{C)}- \quad \begin{array}{c} R_5 \\ | \\ O=C \\ | \\ R_6 \end{array}$$

formula (4)

$$-\text{(CH}_2-\text{C)}- \quad \begin{array}{c} R_7 \\ | \\ O=C \\ | \\ R_8 \end{array}$$
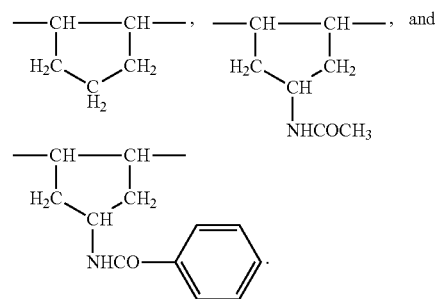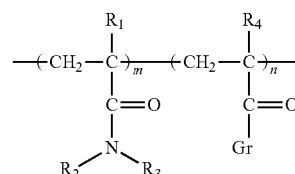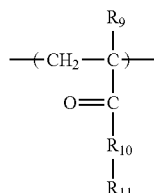
wherein in formula (3), R_5 is H or a methyl group; R_6 is a radical selected from the group consisting of the structures of formula (5) and formula (6),

formula (5)

$$CH_2-O(CH_2)_aCH_3$$
$$CH_2-O-CH$$
$$CH_2-O(CH_2)_aCH_3$$
$$-O-CH$$
$$CH_2-O(CH_2)_aCH_3$$
$$CH_2-O-CH$$
$$CH_2-O(CH_2)_aCH_3,$$

formula (6)

$$CH_2-O(CH_2)_2COOCH_2CH_3$$
$$-NH-C-CH_2-O(CH_2)_2COOCH_2CH_3,$$
$$CH_2-O(CH_2)_2COOCH_2CH_3$$

wherein in formula (5), a is an integer from 1 to 11, and

wherein in formula (4), R_7 is H or a methyl group; R_8 is selected from the group consisting of —NHPhOH, —OCH$_2$Ph, —OPhOH, —OPhCOOH and salts thereof, —NHC(CH$_3$)$_2$CH$_2$SO$_3$H and salts thereof, —OC(CH$_3$)$_2$(CH$_2$)$_b$CH$_3$, —NHC(CH$_3$)$_2$(CH$_2$)$_c$CH$_3$, —OC(CH$_3$)$_2$CH$_2$C(CH$_3$)$_2$(CH$_2$)$_d$CH$_3$, —NHC(CH$_3$)$_2$CH$_2$C(CH$_3$)$_2$(CH$_2$)$_e$CH$_3$, —O(CH$_2$)$_f$N$^+$(CH$_3$)$_2$CH$_2$PhX$^-$,

$$-O-(CH_2)_{12}-N^+ \text{(pyridine ring)} Br^-, \text{ and}$$

$$-O- \text{(quinoline ring with Cl)};$$

and

wherein b and c are integers from 0 to 21, respectively; d and e are integers from 0 to 17 respectively; f is an integer from 2 to 8; and X$^-$ is Cl$^-$ or Br.

2. The amphiphilic macromolecule as claimed in claim **1**, wherein the structural unit A for adjusting the molecular weight, molecular weight distribution and charge characteristics comprises a (meth)acrylamide monomer unit A$_1$ and a (meth)acrylic monomer unit A$_2$.

3. The amphiphilic macromolecule as claimed in claim **1**, wherein the amphiphilic structural unit C has a structure of formula (8):

formula (8)

$$R_9$$
$$-(CH_2-C)-$$
$$O=C$$
$$R_{10}$$
$$R_{11}$$

wherein in formula (8), R$_9$ is H or a methyl group; R$_{10}$ is —O— or —NH—; R$_{11}$ is a radical containing a straight-chain hydrocarbyl, a branched hydrocarbyl, a polyoxyethylene (PEO), a polyoxypropylene (PPO), an EO-PO block, a mono-quaternary ammonium salt, a multiple-quaternary ammonium salt, or a sulfonic acid and salts thereof.

4. The amphiphilic macromolecule as claimed in claim **2**, wherein based on 100 mol % of the entire amphiphilic macromolecule repeating units, the molar percentage of the

(meth)acrylamide monomer unit A$_1$ is 70-99 mol %; and the molar percentage of the (meth)acrylic monomer unit A$_2$ is 1-30 mol %.

5. The amphiphilic macromolecule as claimed in claim **1**, wherein based on 100 mol % of the entire amphiphilic macromolecule repeating units, the molar percentage of the structure G is 0.02-2 mol %; and the molar percentage of the structure of formula (4) is 0.05-5 mol %.

6. The amphiphilic macromolecule as claimed in claim **3**, wherein based on 100 mol % of the entire amphiphilic macromolecule repeating units, the molar percentage of the structure of formula (8) is 0.05-10 mol %.

7. The amphiphilic macromolecule as claimed in claim **1**, wherein the structural unit A for adjusting molecular weight, molecular weight distribution and charge characteristics has a structure of formula (2):

formula (2)

$$-(CH_2-C)_m-(CH_2-C)_n-$$
$$R_1 \quad R_4$$
$$C=O \quad C=O$$
$$N \quad Gr$$
$$R_2 \quad R_3$$

wherein in formula (2), R$_1$ is H or a methyl group; R$_2$ and R$_3$ are independently selected from the group consisting of H and a C$_1$-C$_3$ alkyl group; R$_4$ is selected from the group consisting of H and a methyl group; Gr is —OH or —O$^-$Na$^+$; m and n represent the molar percentages of the structural units in the entire amphiphilic macromolecule, and m is from 70 to 99 mol %; n is from 1 to 30 mol %.

8. The amphiphilic macromolecule as claimed in claim **2**, wherein the cyclic hydrocarbon structure formed on the basis of the two adjacent carbon atoms in the main chain is selected from the group consisting of:

$$-CH-CH-, \quad -CH-CH-, \text{ and}$$
$$H_2C \quad CH_2 \quad H_2C \quad CH_2$$
$$C \quad CH$$
$$H_2 \quad NHCOCH_3$$

$$-CH-CH-$$
$$H_2C \quad CH_2$$
$$CH$$
$$NHCO-\text{(phenyl)}.$$

9. The amphiphilic macromolecule as claimed in claim **1**, wherein the highly sterically hindered structural unit B has a structure of formula (7):

formula (7)

$$-(G)_x-(CH_2-C)_y-$$
$$R_7$$
$$O=C$$
$$R_8$$

wherein in formula (7); the definitions on R$_7$ and R$_8$ are as described in formula (4); x and y respectively represent molar percentages of the structural units in the entire amphiphilic macromolecule, and x is from 0.02 to 2 mol %, y is from 0.05 to 5 mol %.
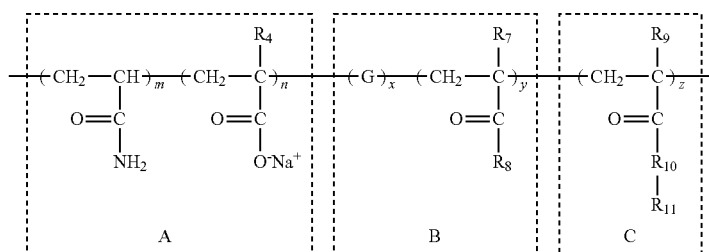
10. The amphiphilic macromolecule as claimed in claim **3**, wherein in formula (8), R_{10} and R_{11} may be selected from the group consisting of $-O(CH_2)_gN^+(CH_3)_2(CH_2)_hCH_3X^-$, $-NH(CH_2)_iN^+(CH_3)_2(CH_2)_jCH_3X^-$, $-O(CH_2)_kN^+((CH_2)_p CH_3)_pX^-$, $-O(CH_2)_qN^+(CH_3)_2(CH_2)_\alpha CH(SO_3H)CH_2 (EO)_\beta(PO)_\gamma(CH_2)_\delta CH_3X^-$, $-NH(CH_2)_qN^+(CH_3)_2(CH_2)_\alpha CH(SO_3H)CH_2(EO)_\beta(PO)_\gamma(CH_2)_\delta CH_3X^-$, $-O(CH_2)_qN^+ (CH_3)_2(CH_2)_\alpha CH(COOH)CH_2(EO)_\beta(PO)_\gamma(CH_2)_\delta CH_3X^-$, $-NH(CH_2)_qN^+(CH_3)_2(CH_2)_\alpha CH(COOH)CH_2(EO)_\beta(PO)_\gamma (CH_2)_\delta CH_3X^-$, $-O(CH_2)_2N^+(CH_3)_2(CH_2)_\epsilon SO_3^-$, $-(OCH (CH_2N^+(CH_3)_2(CH_2)_\zeta CH_3Cl^-)CH_2)_\eta O(CH_2)_\theta CH_3$, $-(OCH(CH_2N^+((CH_2)_\lambda CH_3)_3Cl^-)CH_2)_\iota O(CH_2)_\kappa CH_3$, $-OCH(CH_2N^+(CH_3)_2(CH_2)_r CH_3X^-))_2$, $-OCH(CH_2N^+ ((CH_2)_s CH_3)_3X^-))_2$;

wherein g, i, k and q are respectively integers from 1 to 6; h and j are respectively integers from 3 to 21; p is an integer from 3 to 9; a is an integer from 1 to 12; β and γ are respectively integers from 0 to 40; δ is an integer from 0 to 21; c is an integer from 4 to 18; ζ is an integer from 1 to 21; 11 and η are respectively integers from 1 to 30; θ and κ are respectively integers from 3 to 21; λ is an integer from 0 to 9; r is an integer from 3 to 21; s is an integer from 3 to 9; and X^- is Cl^- or Br^-.

11. The amphiphilic macromolecule as claimed in claim **1**, wherein the amphiphilic macromolecule has a structure of formula (9):
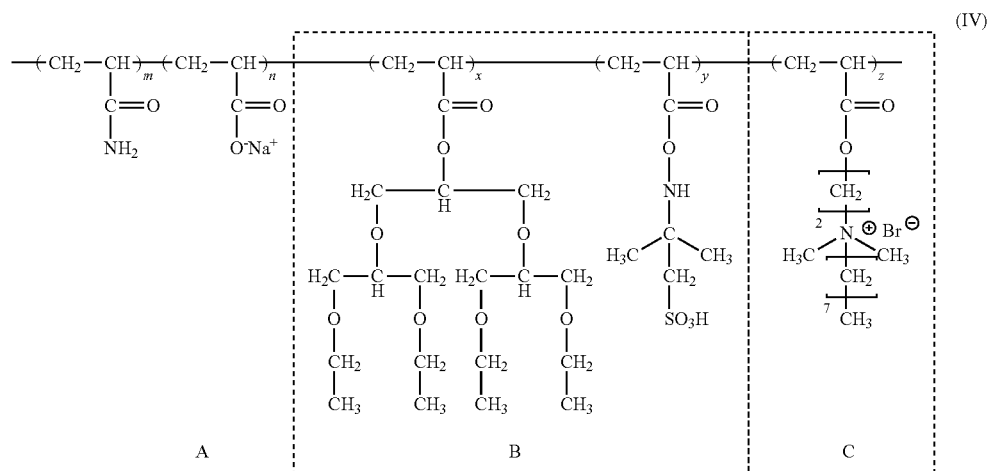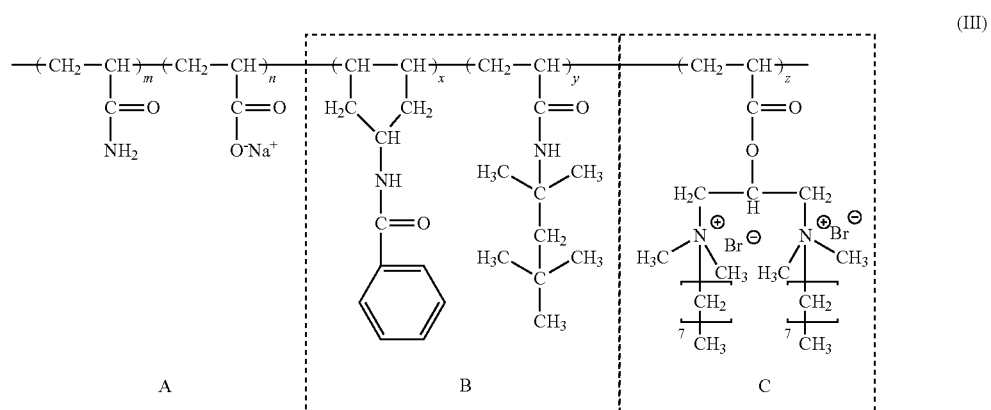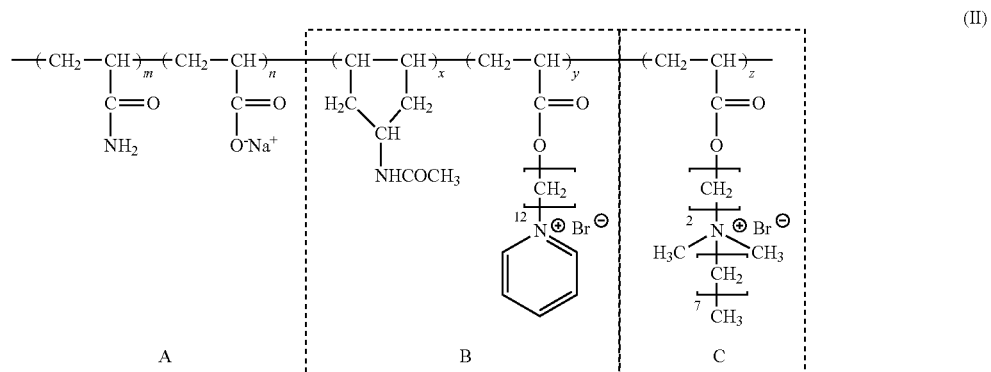
formula (9)

wherein in formula (9), R_4 is selected from the group consisting of H and a methyl group; m and n represent the molar percentages of the structural units in the entire amphiphilic macromolecule, and m is from 70 to 99 mol %; n is from 1 to 30 mol %; the definitions of G, R_7, R_8, x and y are as described in formula (7); R_9 is H or a methyl group, R_{10} is $-O-$ or $-NH-$; R_{11} is a radical containing a straight-chain hydrocarbyl, a branched hydrocarbyl, a polyoxyethylene (PEO), a polyoxypropylene (PPO), an EO-PO block, a mono-quaternary ammonium salt, a multiple-quaternary ammonium salt, or a sulfonic acid and salts thereof; z represents the molar percentage of the structural unit in the entire amphiphilic macromolecule, and z is from 0.05 to 10 mol %.
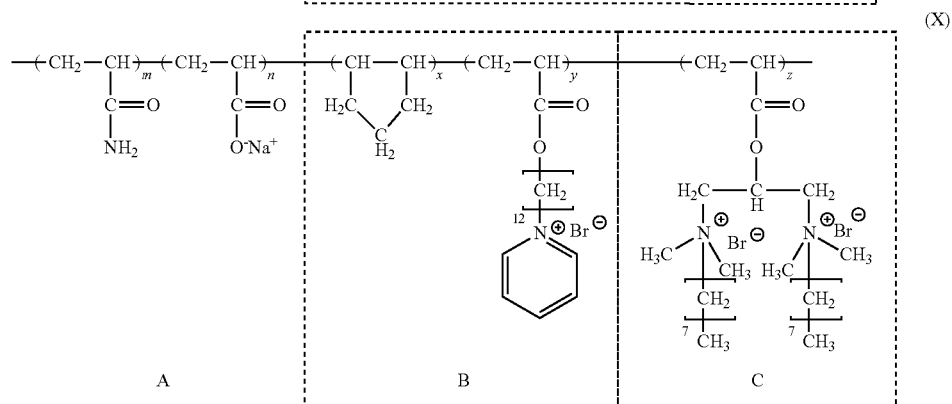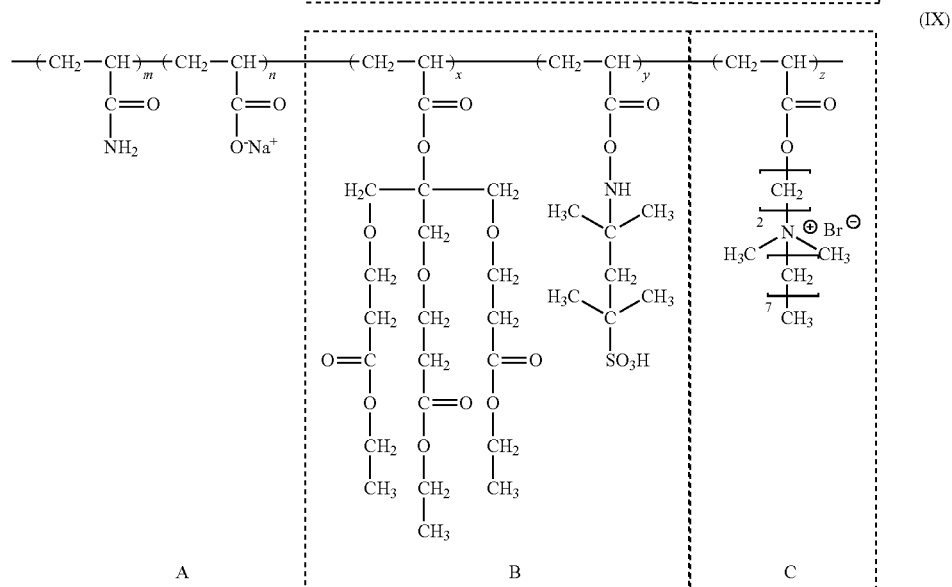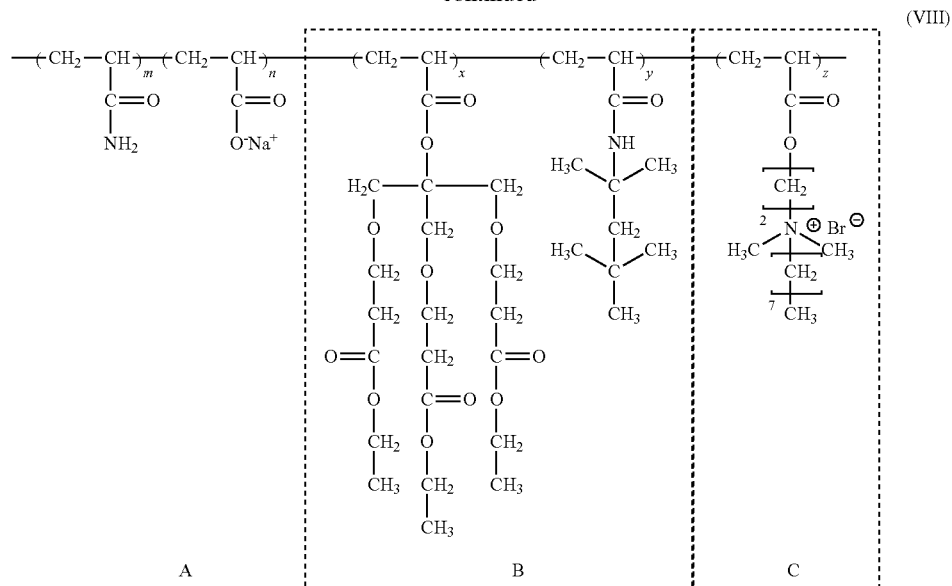
12. The amphiphilic macromolecule as claimed in claim **1**, which is a compound of formulas (I)-(X):

(I)

(II)

A   B   C

(III)

A   B   C

(IV)

A   B   C

(V)

A   B   C

(VI)

A   B   C

(VII)

A   B   C

-continued

(VIII)

A   B   C

(IX)

A   B   C

(X)

A   B   C
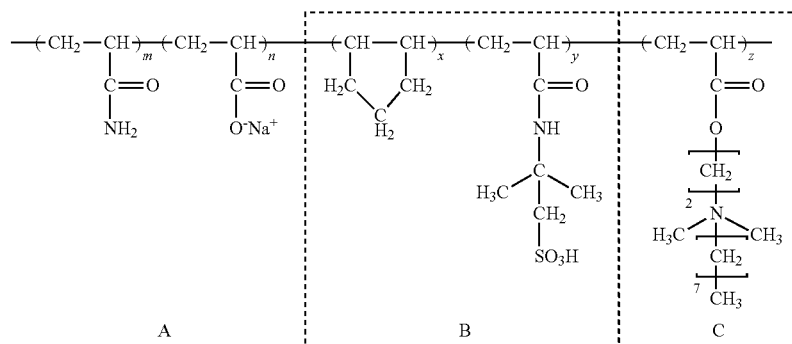
wherein m, n, x, y, and z in formulae (I) to (X) respectively represent the molar percentages of the structural units in the entire amphiphilic macromolecule, in which, m is from 70 to 99 mol %; n is from 1 to 30 mol %; x is from 0.02 to 2 mol %, y is from 0.05 to 5 mol %, and z is from 0.05 to 10 mol %.

13. The amphiphilic macromolecule as claimed in claim **1**, wherein the amphiphilic macromolecule has a molecular weight of between 1000000-20000000.

14. A method comprising:

formulating the amphiphilic macromolecule as claimed in claim **1** into an aqueous solution; and

utilizing the aqueous solution in oilfield drilling, well cementing, fracturing, crude oil gathering and transporting, sewage treating, sludge treating and papermaking as intensified oil producing agent and oil displacing agent, or as a heavy oil viscosity reducer, fracturing fluid component, clay stabilizer, sewage treating agent, retention aid and drainage aid or strengthening agent for papermaking.

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